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Classical Nucleation Theory Description of Active Colloid Assembly

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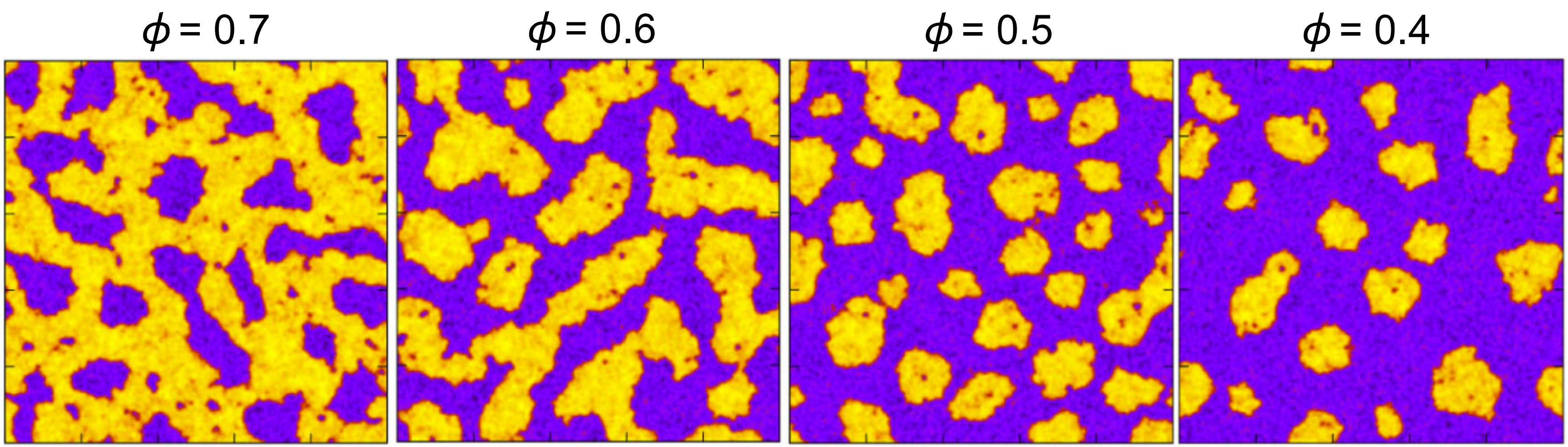
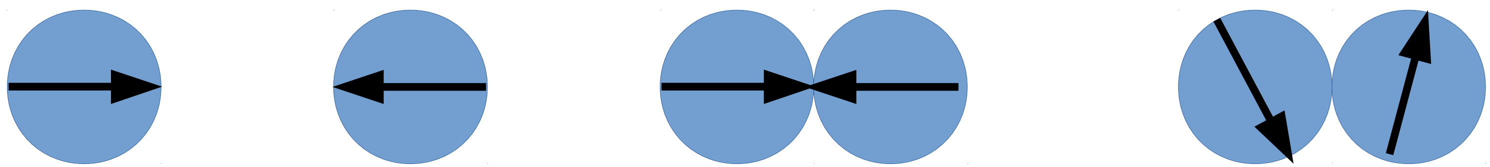


$$\dot{\boldsymbol{r}}_i = \boldsymbol{F}(\{\boldsymbol{r}_i\})/\xi + v_{\mathrm{p}}\hat{\boldsymbol{\nu}}_i + \sqrt{2D}\boldsymbol{\eta}_i^{\mathrm{T}},$$

$$\dot{\theta}_i = \sqrt{2D_{\mathrm{r}}}\eta_i^{\mathrm{R}}.$$

Phase separation of active particles

- Separation can happen without attraction force



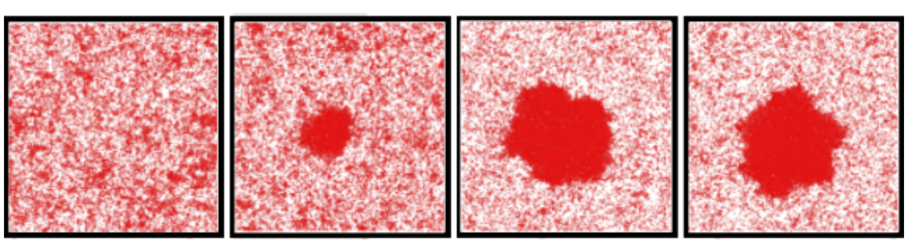
takes time
"effective attraction"

Time scales in the system:
1. diffusion time ~ σ^2/D
2. rotational diffusion time ~ $1/D_r$
3. active ballistic motion ~ σ/v_p

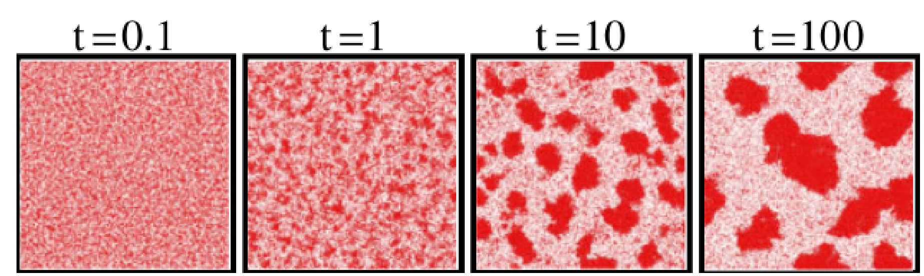
Separation happens if active ballistic motion time >> rotational diffusion time,i.e.

$$1/D_{r/} >> \sigma/v_p$$

- Separation can be:



nucleation



spinodal decomposition
has a theory: Phys. Rev. Lett. 111 145702 (2013)

Can CNT apply?

- ✓ analog to liquid/vapor phase separation of passive particles
- ✓ chemical potential can be well mapped

  Phys. Rev. Lett. 111 145702 (2013)

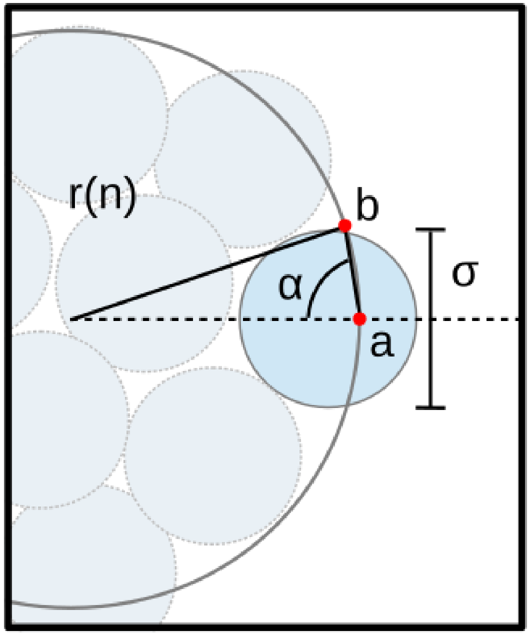
- ✗ non-equilibrium
- ✗ different mechanism
- ✗ no well-defined pressure
- ✗ no well-defined interfacial energy
  - negative mechanical interfacial energy

    Phys. Rev. Lett. 115 098301 (2015)

Yes, CNT applies

Key reasons

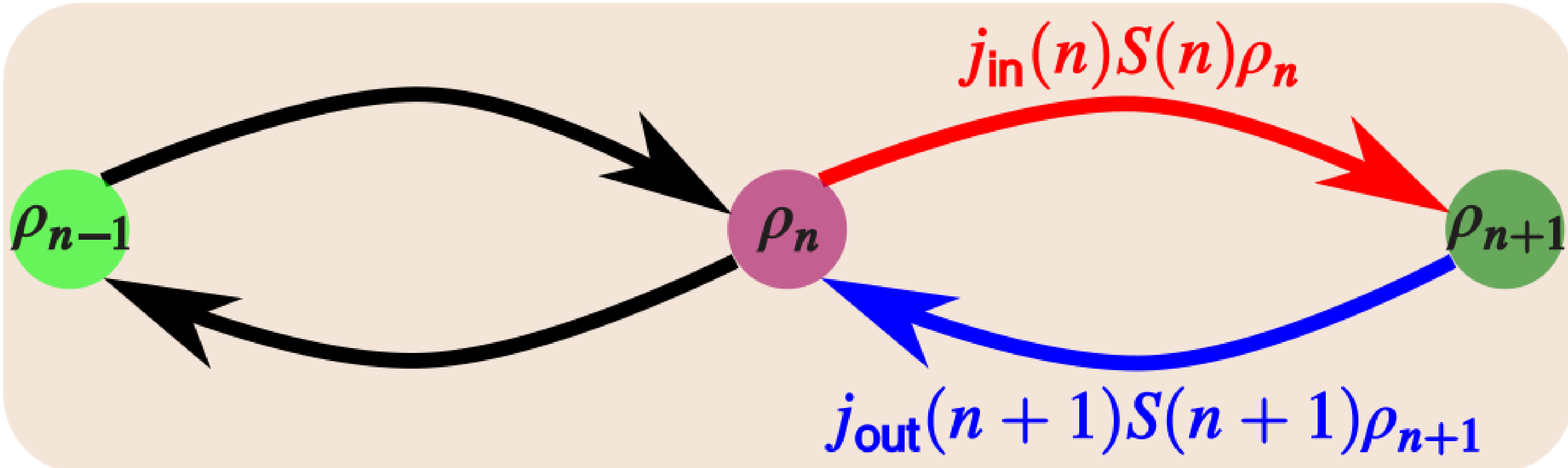
- single reaction coordinate: **nucleus size n**
- curvature-dependent evaporation rate

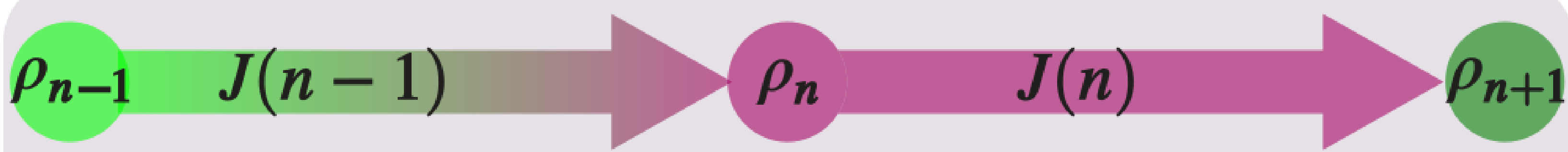


$$j_{out} \sim a - b/r$$

gives rise to an positive effective surface tension

CNT master equation





$J(n)$ = net flux from n to (n+1)

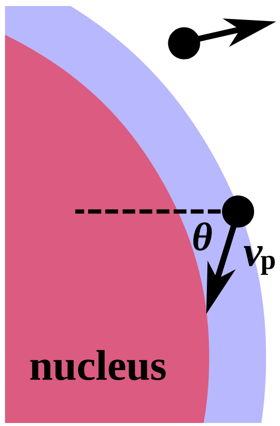
$$\partial_t \rho_n = J(n-1) - J(n)$$

At "equilibrium", J = 0, we have

$$\rho_n = \rho_1 \prod_{m=1}^{n-1} \frac{j_{\text{in}}(m)S(m)}{j_{\text{out}}(m+1)S(m+1)} \equiv \rho_1 P(n)$$

Absorption and evaporation rate

$$j_{\text{in}} = (\rho_{\text{g}} v_{\text{p}} / \pi)$$

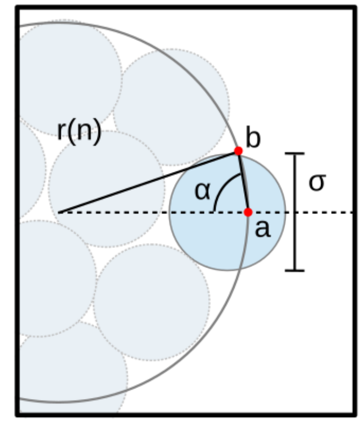


Mechanism:
- v_p transports particles to the surface

Assumptions:
- Large nucleus, i.e. flat surface
- Pe >> 1, i.e. v_p dominates

$$j_{\text{out}}(n) = (D_{\text{r}}/\sigma)[\pi/2\alpha(n)]^2$$

$$\alpha(n) = \frac{1}{2}[\pi - \sin^{-1}(\sigma)/2r(n)]$$



Mechanism:
- *direction of* v_p diffuses and kicks particles out

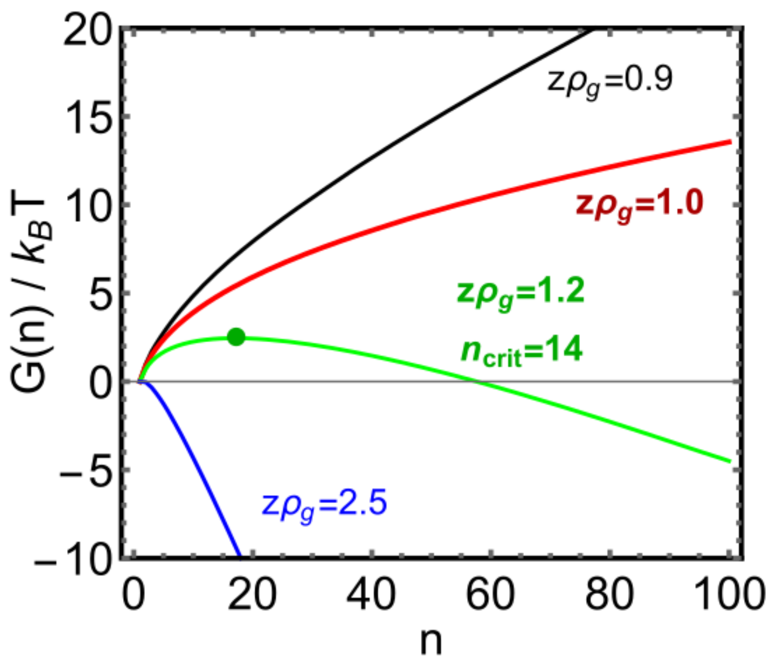
Assumptions:
- Large nucleus, i.e. relatively flat surface
- Pe >> 1, i.e. v_p dominates

Steady-state cluster size distribution

$$\rho_n \propto \exp\left[-G(n)/(k_\mathrm{B}T)\right]$$

$$G(n) = -k_\mathrm{B}T\left(\ln(z\rho_\mathrm{g})n - \frac{\sigma\rho_\mathrm{c}}{\pi}S(n)\right) + \mathcal{O}(\ln n)$$

bulk surface



$$z = (v_\mathrm{p}\sigma/\pi D_\mathrm{r})$$

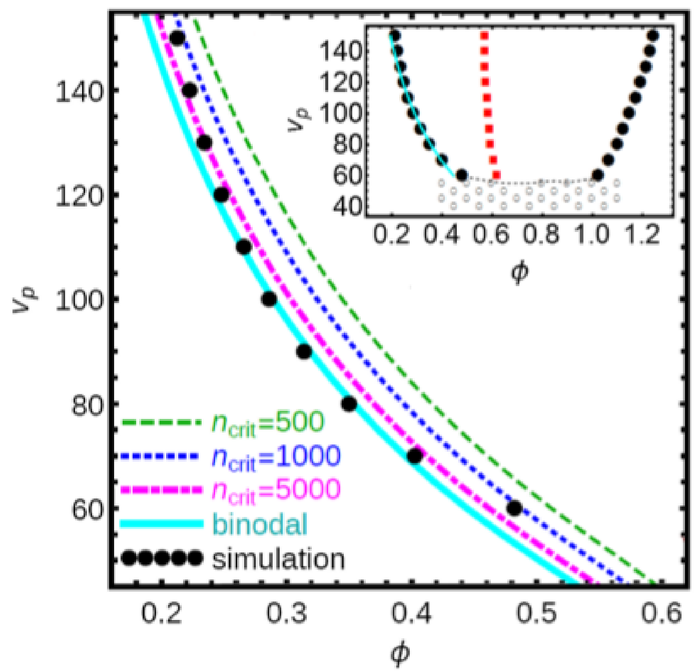
Separation happens if active ballistic motion time >> rotational diffusion time,i.e.

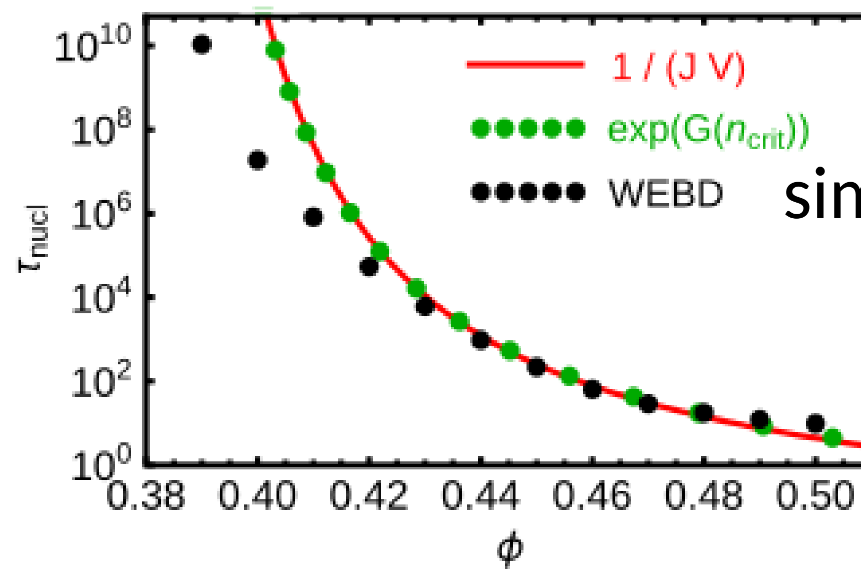
$1/D_{r/} >> \sigma/v_p$

$$\Delta\mu = \ln[(v_\mathrm{p}\sigma/\pi D_\mathrm{r})\rho_\mathrm{g}]$$

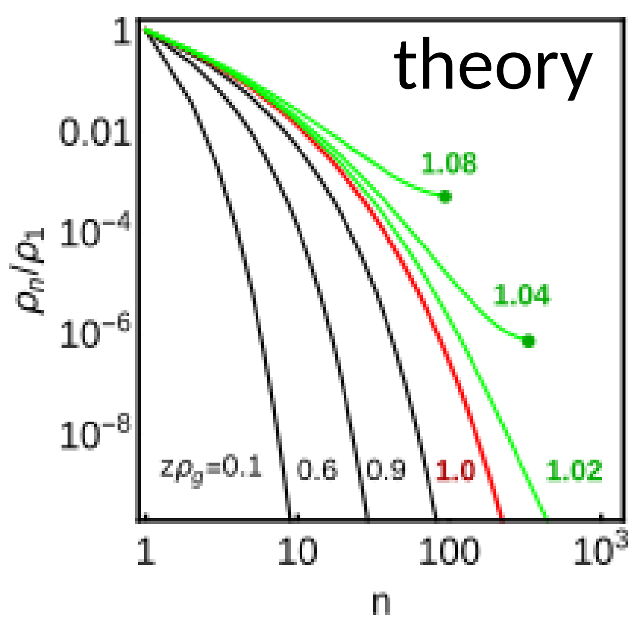
	CNT for passive system	CNT for active system
chemical potential	density	density, v_p, D_r
surface tension	excess free energy to create surface	curvature-dependent flux ~ a – b/r
barrier mechanism	competition of bulk and surface terms	competition of absorption and evaporation (time scale separation)
has free-energy?	yes	no, but effectively yes
can predict spinodal line?	no	yes, but wrong
works for any dimension?	yes	principally yes

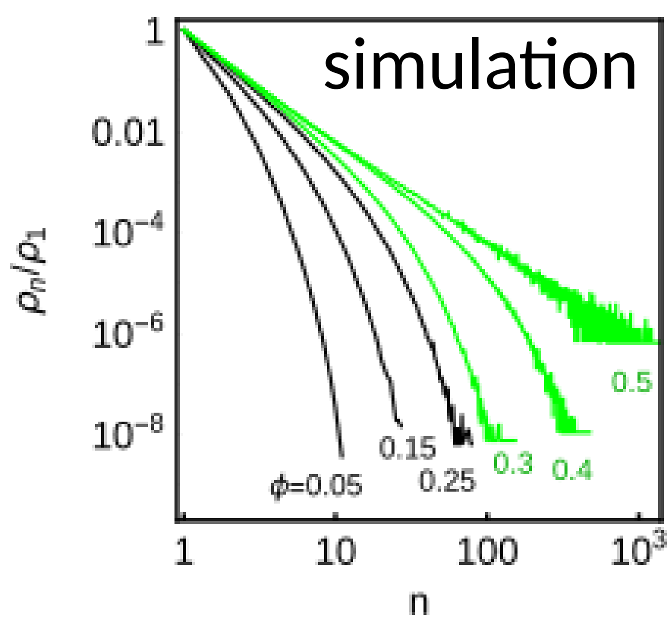
Prediction and verification





theory
simulation





Outlook

- CNT for nucleation under shear
- Surface premelting of crystal with purely repulsive active particles
  - crystal has been observed